

Finite-Size Effects in Surface-Enhanced Raman Scattering from Molecules Adsorbed on Noble-Metal Nanoparticles

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We study the role of strong electron confinement in surface-enhanced Raman scattering from molecules adsorbed on small noble-metal particles. We describe a new source of Raman signal enhancement which originates from different behavior of *sp*-band and *d*-band electron densities near the particle boundary. In small particles, a spillover of *sp*-electron wave-functions beyond the classical radius gives rise to a thin layer with diminished population of *d*-electrons. In this surface layer, the screening of *sp*-electrons by *d*-band electron background is reduced. We demonstrate that the interplay between finite-size and underscreening effects results in an increase of the surface plasmon local field acting on a molecule located in a close proximity to the particle boundary. Our calculations, based on two-region model, show that the additional enhancement of Raman signal gets stronger for smaller nanoparticles due to a larger volume fraction of underscreened region.

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I. INTRODUCTION

A renewed interest in surface-enhanced Raman scattering (SERS)[1, 2] stems from the discovery of an enormous (up to 10^{15}) enhancement of single-molecule Raman signal in silver nanoparticle aggregates [3, 4]. Although the relative importance of various mechanisms of SERS is still an issue under active discussion, the main source is attributed to the electromagnetic enhancement due to the local field of surface plasmon (SP) excited in a nanoparticle by the incident light [5, 6, 7, 8] (see Fig. 1). Other possible enhancement mechanisms involve dynamical charge transfer between a nanoparticle and a molecule (chemical mechanism) and have been addressed, e.g., in Refs. [9, 10, 11, 12]. Recent experimental [13, 14, 15, 16, 17] and theoretical [18, 19, 20, 21, 22] studies indicate that the anomalously strong Raman signal originates from “hot spots” – spatial regions where clusters of several closely-spaced nanoparticles are concentrated in a small volume. The high-intensity SERS then originates from the mutual enhancement of SP local electric fields of several nanoparticles that determine the dipole moment of a molecule trapped in a gap between metal surfaces.

Although in *single* nanoparticles the magnitude of SERS is considerably smaller, with enhancement up to 10^6 relative to the Raman crosssection of an isolated molecule, it varies substantially with nanoparticles shape and size. In spheroidal particles, a strong local field enhancement near the tip [7] leads to a lightning rod effect recently observed in SERS from nanorods [23]. In gold nanorods [24] and nanoshells [25], an additional local field enhancement comes from a redshift of the SP energy away from the onset of optical transitions between electronic *d*-band and *sp*-band. However, in spherical Au particles, the proximity of SP and interband transitions energies leads to a damping of SP by interband electron excitations and, thus, to a reduction of the SP local field.

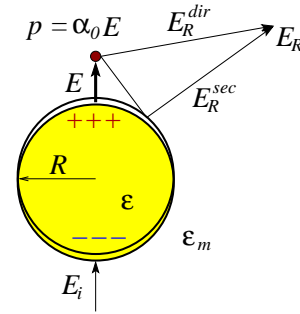


FIG. 1: Schematic representation of SERS from a molecule adsorbed on a metal nanoparticle.

Such a damping is even stronger in Cu nanoparticles, where the SP energy lies above the interband transitions onset [26]. In silver particles, however, the interband transitions onset lies considerably higher in energy (~ 4.0 eV) than the SP (~ 3.0 eV for nanoparticles in, e.g., glass matrix) and have very little detrimental effect on SERS.

Virtually all theoretical studies of the electromagnetic mechanism of SERS were performed for relatively large nanoparticles with diameters of several dozens nm or larger. For such sizes, the SP damping rate, γ , in Ag particles comes mainly from the electron-phonon scattering or electromagnetic retardation effects (for larger particles). However, for particle sizes smaller than ~ 10 nm, the finite-size effects become important. For small particles, the width of the resonance peak in absorption is determined chiefly by the SP damping due to excitation of high-energy *intra*band single-particles transitions accompanied by transfer of momentum to nanoparticle boundary [27]. This effect is usually incorporated via size-dependent correction, $\gamma = \gamma_0 + \gamma_s$, in the Drude dielectric function for *sp*-electrons,

$$\epsilon_s(\omega) = 1 - \omega_p^2 / \omega(\omega + i\gamma), \quad (1)$$

where ω_p is the bulk plasmon frequency ($\omega_p \simeq 9.0$ eV for Ag), and γ_s is determined by the electron level spacing near the Fermi level,

$$\gamma_s \sim v_F/R, \quad (2)$$

with a numerical coefficient of the order of unity (we set $\hbar = 1$). For small particles, γ_s dominates over the phonon-induced damping, γ_0 , resulting in a strong dependence of SERS on nanoparticle size. Indeed, the amplitude of the SP local field *at resonance* is $E \propto \gamma^{-1}$, so that the electromagnetic enhancement factor [6] depends on the radius as $A(\omega) = |E/E_i|^4 \propto R^4$ (here E_i is the incident field). Thus, in small particles, finite size effects can reduce SERS by several orders of magnitude.

In this paper, we demonstrate that for even smaller nanometer-sized particles, another quantum-size effect, with the opposite trend towards *increasing* SERS, becomes important. The underlying mechanism is related to the difference in the density profiles of *sp*-band and *d*-band electrons near the nanoparticle boundary. Specifically, the *localized d*-electrons are mainly confined within nanoparticle classical volume while the wave-functions of *delocalized sp*-electrons extend outside of it. This spillover leads to a larger *effective* radius for *sp*-electrons [28] and, thus, to the existence of a surface layer with diminished *d*-electron population [29, 30, 31]. As a result, in the surface layer, the screening of *sp*-electrons by *d*-band electron background is reduced, leading to a blueshift of SP absorption peak in small Ag nanoparticles. More recently, the effect of underscreening of Coulomb interactions between *sp*-electrons has been observed as an enhancement of electron-electron scattering rate measured in ultrafast pump-probe spectroscopy [32, 33] and photoemission [34] experiments.

Specifically, we address the role underscreening plays in the SERS from a molecule located in a close proximity to the surface of an Ag nanoparticle. We find a substantial increase of the SP local field *outside* of nanoparticle and, hence, an additional enhancement of the Raman signal. Furthermore, we investigate the size-dependence of SERS to find that the enhancement factor deviates considerably from the R^4 behavior when the screening effects are included. In particular, the relative enhancement is stronger for smaller nanoparticles due to a larger volume fraction of the underscreened region.

The paper is organized as follows. In Section II we describe the two-region model which we adopt to incorporate the surface layer effect. In Section III we calculate local fields and Raman enhancement factor. Discussion of our numerical results is presented in Section IV. Section V concludes the paper.

II. MODEL

We consider SERS from a molecule adsorbed on a Ag nanoparticle in a medium with dielectric constant ϵ_m . For nanoparticle diameters exceeding ≈ 1.5 nm,

the bulk electronic structure is essentially preserved while the quantum-mechanical corrections due to discreteness of the electron energy spectrum can be included via γ_s in the *sp*-electron dielectric function Eq. (1). To incorporate the surface layer effect, we adopt the two-region model where *sp*-band and *d*-band electrons are confined within spherical volumes with different radii R_d and R , respectively [29, 30, 35]. Note that for *d*-band electrons, the semiclassical approach [35] remains valid even for smaller nanometer-sized particles [30], while for *sp*-electrons, the density $n_s(r)$ is a smooth function near the boundary while exhibiting Friedel oscillations inside the nanoparticles [36]. A fully quantum-mechanical theory of SERS in nanometer-sized particles will be published elsewhere [37]. For nanoparticles under consideration, however, the deviations of *sp*-electron density from classical shape do not affect the situation qualitatively [29] and $n_s(r)$ can be approximated by a step-function with a sharp boundary at the effective radius R .

The frequency-dependent potential is determined from the Poisson equation,

$$\Phi(\omega, \mathbf{r}) = \phi_0(\mathbf{r}) + \int d^3r' \frac{\delta N(\omega, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3)$$

where $\phi_0(\mathbf{r}) = -e\mathbf{E}_i \cdot \mathbf{r}$ is the potential of incident light with electric field amplitude $\mathbf{E}_i = E_i \mathbf{z}$ along the *z*-axis, and $\delta N(\omega, \mathbf{r})$ is the induced charge density (hereafter we suppress the frequency dependence). The latter has four contributions,

$$\delta N(\mathbf{r}) = \delta N_s(\mathbf{r}) + \delta N_d(\mathbf{r}) + \delta N_m(\mathbf{r}) + \delta N_0(\mathbf{r}), \quad (4)$$

originating from the valence *sp*-electrons, the core *d*-electrons, the dielectric medium, and the molecule, respectively. The density profile of delocalized *sp*-electrons is not fully inbedded in the background of localized *d*-electrons but extends over it by $\Delta = R - R_d$ which, within our model, is the surface layer thickness [29, 30, 35]. The induced density is expressed via electric polarization vector as

$$\delta N(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r}) = -\nabla \cdot (\mathbf{P}_d + \mathbf{P}_s + \mathbf{P}_m + \mathbf{P}_0), \quad (5)$$

with each contribution related back to the potential as

$$\begin{aligned} \mathbf{P}_d(\mathbf{r}) &= -\frac{\epsilon_d - 1}{4\pi} \theta(R_d - r) \nabla \Phi(\mathbf{r}), \\ \mathbf{P}_s(\mathbf{r}) &= -\frac{\epsilon_s - 1}{4\pi} \theta(R - r) \nabla \Phi(\mathbf{r}), \\ \mathbf{P}_m(\mathbf{r}) &= -\frac{\epsilon_m - 1}{4\pi} \theta(r - R) \nabla \Phi(\mathbf{r}), \\ \mathbf{P}_0(\mathbf{r}) &= -\delta(\mathbf{r} - \mathbf{r}_0) \alpha_0 \nabla \Phi(\mathbf{r}_0), \end{aligned} \quad (6)$$

where step functions $\theta(x)$ enforce the corresponding boundary conditions. The molecule is represented by a point dipole with polarizability α_0 located at \mathbf{r}_0 (we chose nanoparticle center as the origin). In the following, averaging over the orientations of molecular dipole

is implied so the polarizability tensor α_0 is assumed to be isotropic.

After substituting above expressions into r.h.s. of Eq. (3) and integrating by parts, we obtain a self-consistent equation for the potential $\Phi(\mathbf{r})$,

$$\begin{aligned} \epsilon(r)\Phi(\mathbf{r}) = & \phi_0(\mathbf{r}) - \nabla_0 \frac{1}{|\mathbf{r} - \mathbf{r}_0|} \cdot \alpha_0 \nabla_0 \Phi(\mathbf{r}_0) \\ & + \int d^3r' \nabla' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \nabla' [\chi_d \theta(R_d - r') \\ & + \chi_s \theta(R - r') + \chi_m \theta(r' - R)] \Phi(\mathbf{r}'), \end{aligned} \quad (7)$$

where $\epsilon(r) = \epsilon_d + \epsilon_s - 1$, ϵ_s , and ϵ_m in the intervals $r < R_d$, $R_d < r < R$, and $r > R$, respectively, and $\chi_i = (\epsilon_i - 1)/4\pi$ ($i = s, d, m$) are the corresponding susceptibilities. For simplicity, we assume that the molecule is located on the z -axis (along incident field direction). After expanding $\Phi(\mathbf{r})$ and $|\mathbf{r} - \mathbf{r}'|^{-1}$ in terms of spherical harmonics and retaining only the dipole terms, we obtain for the radial component

$$\begin{aligned} \epsilon(r)\Phi(r) = & \phi_0(r) - \frac{\epsilon_d - 1}{3} \beta\left(\frac{r}{R_d}\right) \Phi(R_d) \\ & + \frac{\epsilon_m - \epsilon_s}{3} \beta\left(\frac{r}{R}\right) \Phi(R) \\ & - \frac{4\pi\alpha_0}{3r_0^2} \beta\left(\frac{r}{r_0}\right) \frac{\partial\Phi(r_0)}{\partial r_0}, \end{aligned} \quad (8)$$

where

$$\beta(x) = x^{-2} \theta(x - 1) - 2x\theta(1 - x). \quad (9)$$

The second and third terms in rhs of Eq. (8) describe light scattering from the boundaries at $r = R_d$ and $r = R$, respectively, that separate regions with different dielectric functions, while the last term represents the potential of the molecular dipole. The boundary values of Φ are found by setting $r = R_d, R, r_0$ in Eq. (8), which leads to a closed-form expression for the self-consistent potential in the presence of molecule, nanoparticle, and dielectric medium.

III. CALCULATION OF RAMAN SIGNAL

The dipole moment of a radiating molecular dipole is determined by the local electric field, \mathbf{E} , at the molecule location: $\mathbf{p} = \alpha_0 \mathbf{E}$. The Raman field consists of a direct field of this dipole and a secondary field scattered by the nanoparticle. In order to extract the Raman signal, we present the self-consistent potential in the form $\Phi = \phi + \phi^R$, where ϕ is the local potential in the absence of molecule and ϕ^R , calculated in the first order in α_0 , determines the Raman signal [8].

Keeping only zero-order terms in Eq. (8), we find for

the nanoparticle local potential

$$\begin{aligned} \phi = \phi_0 + \delta\phi, \quad \phi_0 = \phi_0/\epsilon(r) = -E_i r/\epsilon(r), \\ \delta\phi(r) = \frac{1}{\epsilon(r)} \left[-\beta(r/R_d) \phi_0(R_d) \frac{\lambda_d(1 - 2\lambda_m)}{1 - 2a^3\lambda_d\lambda_m} \right. \\ \left. + \beta(r/R) \phi_0(R) \frac{\lambda_m(1 - a^3\lambda_d)}{1 - 2a^3\lambda_d\lambda_m} \right], \end{aligned} \quad (10)$$

where $a = R_d/R$ is the ‘‘aspect ratio’’, and the parameters λ_d and λ_m are given by

$$\lambda_d = \frac{\epsilon_d - 1}{\epsilon_d + 3\epsilon_s - 1}, \quad \lambda_m = \frac{\epsilon_m - \epsilon_s}{2\epsilon_m + \epsilon_s}. \quad (11)$$

The spatial dependence of induced potential, $\delta\phi$, is determined by $\beta(x)$ of Eq. (9). Inside the particle, the potential linearly increases for $r < R_d$, while it exhibits a more complicated behavior in the surface layer, $R_d < r < R$. Outside the nanoparticle, $\delta\phi$ falls off quadratically,

$$\delta\phi(r) = \frac{E_i \alpha}{\epsilon_m r^2}, \quad r > R, \quad (12)$$

where $\alpha(\omega)$ is the particle polarizability

$$\alpha(\omega) = R^3 \frac{a^3 \lambda_d (1 - \lambda_m) - \lambda_m}{1 - 2a^3 \lambda_d \lambda_m}. \quad (13)$$

In the absence of the surface layer, $R_d = R$, we recover the usual expression

$$\alpha^0 = R^3 \frac{\epsilon_s + \epsilon_d - 1 - \epsilon_m}{\epsilon_s + \epsilon_d - 1 + 2\epsilon_m}, \quad (14)$$

with the resonance at $\omega_M = \frac{\omega_p}{\sqrt{\epsilon_d + 2\epsilon_m}}$. From Eqs. (10) and (12), we then obtain the local electric field at the molecule location as

$$E(r_0) = -\frac{\partial\phi}{\partial r_0} = \frac{E_i}{\epsilon_m} (1 + 2g), \quad g(\omega) = \frac{\alpha(\omega)}{r_0^3}. \quad (15)$$

To calculate the Raman signal, we substitute the local field into the last term of Eq. (8) and, in the first order in α_0 , obtain the following equation for ϕ^R ,

$$\begin{aligned} \epsilon(r)\phi^R(r) = & \phi_0^R(r) - \frac{\epsilon_d - 1}{3} \beta(r/R_d) \phi^R(R_d) \\ & + \frac{\epsilon_m - 1}{3} \beta(r/R) \phi^R(R), \end{aligned} \quad (16)$$

where the potential

$$\phi_0^R(r) = \frac{4\pi\alpha'_0}{3r_0^2} E(r_0) \left[\frac{r_0^2}{r^2} \theta(r - r_0) - \frac{2r}{r_0} \theta(r_0 - r) \right], \quad (17)$$

describes the direct field of a radiating molecular dipole (α'_0 is the derivative of molecule polarizability with respect to normal coordinate that determines the Stokes shift ω_S [38]), while the second and third terms describe secondary fields due to scattering from d -band and sp -band electron distributions boundaries, respectively. The

latter can be found by matching ϕ^R at $r = R_d$ and $r = R$. We now notice that, at these values, $\phi_0^R(r)$ is linear in r , so we can write $\phi^R = \varphi_0^R + \delta\varphi_0^R$ with

$$\varphi_0^R = \phi_0^R/\epsilon(r), \quad \delta\phi^R(r) = \frac{8\pi\alpha'_0}{3r_0^3} E(r_0) \delta\varphi(r), \quad (18)$$

where $\delta\varphi(r)$ is given by Eq. (10) but with ω_S instead of ω . We then finally obtain for the Raman field ($r > r_0$)

$$\phi^R(r) = -\frac{4\pi\alpha'_0 E_i}{3\epsilon_m r^2} \left[1 + 2g(\omega)\right] \left[1 + 2g(\omega_s)\right], \quad (19)$$

and, hence, for the enhancement factor

$$A(\omega, \omega_s) = \left|1 + 2g(\omega) + 2g(\omega_s) + 4g(\omega)g(\omega_s)\right|^2. \quad (20)$$

The above expressions generalize the well-known classical result [6, 7, 8] to the case of a small noble-metal particle with different profiles of d -band and sp -band densities. While SERS retains the usual dependence on nanoparticle polarizability, the latter is modified in the presence of a surface layer [see Eq. (13)]. Note that Eq. (19) remains unchanged even for non-classical electron distributions provided that electronic wave-functions in a nanoparticle do not overlap with molecular orbitals [37].

IV. NUMERICAL RESULTS

Below we present the results of numerical calculations for Ag nanoparticles with diameters ranging from 2 to 6 nm in a medium with dielectric constant $\epsilon_m = 2.0$. The SP resonance is positioned at $\omega_M \simeq 3.0$ eV, far away from the interband transitions onset in Ag at 4.0 eV, so in the frequency range of interest the real part of interband dielectric function is nearly a constant, $\epsilon_d \simeq 5.2$. In this size range, the SP damping is dominated by size-dependent contribution to γ , with the numerical coefficient in γ_s [see Eq. (2)] adjusted to fit the experimental absorption data [32].

In Fig. 2, we show calculated absorption spectra for various surface layer thicknesses Δ . For finite thicknesses, the SP energy experiences a blueshift whose magnitude increases with Δ , in agreement with previous calculations of absorption in small silver particles [29, 30]. This blueshift originates from a reduction of the *effective* (averaged over the volume) interband dielectric function in the nanoparticle that determines the SP energy. At the same time, the peak amplitude increases with Δ while the resonance width is unchanged. The absolute value of polarizability determines, in turn, the magnitude of the local field outside the nanoparticle [see Eq. (15)].

In Fig. 3 we plot the local electric field at SP resonance frequency as a function of molecule distance from the metal surface, $d = r - r_0$. Outside the nanoparticle, the local field exhibits the usual r^{-3} decay relative to constant incident field background. At the same time, the field magnitude is larger for finite Δ , reaching $\simeq 20\%$

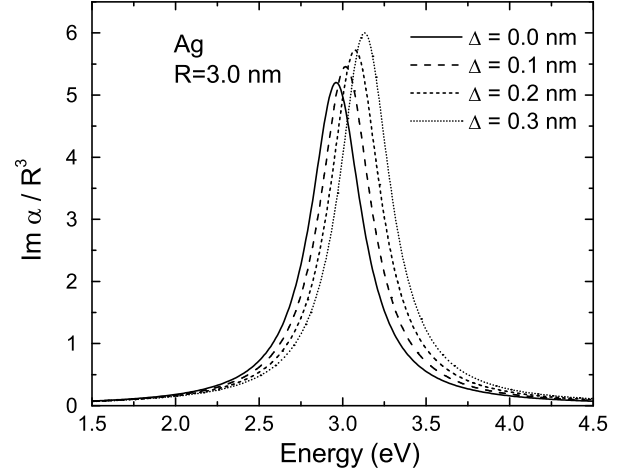


FIG. 2: Absorption spectra of Ag nanoparticle calculated for $R = 3.0$ nm and several values of surface layer thickness Δ .

enhancement near the boundary for 3.0 Å thick surface layer. Enhancement is strongest when the molecule is located in a close proximity to metal surface, near the *underscreened* region with small population of d -electrons.

We now turn to the size-dependence of SERS. In Fig. 4, we plot the enhancement factor at SP energy as a function of particle radius for a small molecule-particle separation $d = 0.1$ nm. We consider here non-resonant scattering and assume, as usual, that molecular vibrational energies lie within SP resonance width (the latter

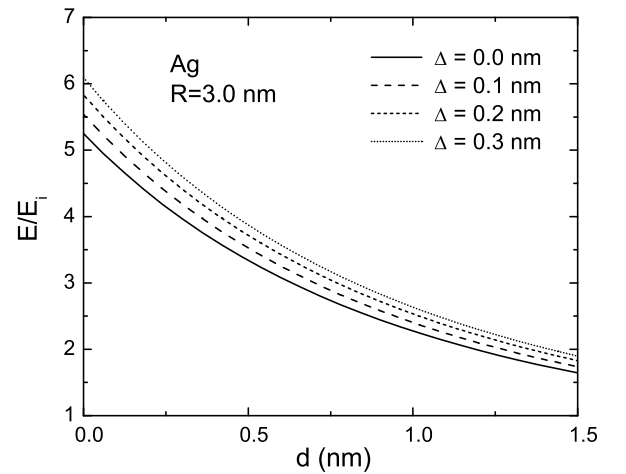


FIG. 3: Local field at surface plasmon energy as a function of distance from particle boundary calculated for $R = 3.0$ nm and several values of surface layer thickness Δ .

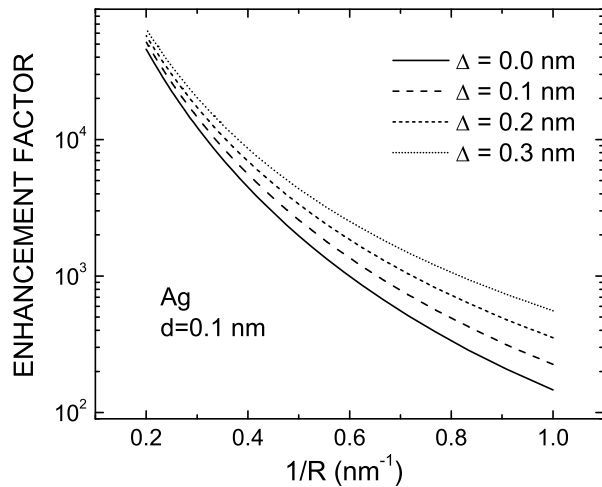


FIG. 4: Size-dependence of Raman enhancement factor calculated for particle-molecule distance $d = 0.1$ nm and several values of surface layer thickness Δ .

being large for nanometer-sized particles). In this case, the main contribution to SERS comes from the last term of Eq. (20) corresponding to the secondary scattered field of radiating molecular dipole. As it can be seen in Fig. 4, the general tendency is a decrease of the Raman signal for small nanoparticles due to a strong SP damping by single-particle excitations. For $\Delta = 0$, the size-dependence of enhancement factor is $A \propto R^4$. However, that dependence changes considerably when the effect of surface layer is included in the calculations. For finite Δ , the decrease of A is considerably slower, with the signal strength in small nanoparticles about 400% larger than that for $\Delta = 0$. It should be emphasized that the role of the surface layer becomes more pronounced when particle size is decreased. Indeed, the *relative* enhancement of SERS is larger for smaller particles [see Fig. 4] due to a larger volume fraction of the underscreened region.

V. CONCLUSIONS

We investigated the role of quantum-size effects in the electromagnetic mechanism of surface-enhanced Raman scattering in noble-metal nanoparticles. We identified a new source of Raman signal enhancement in small particles which originates from different density profiles of *sp*-band and *d*-band electrons near the boundary. The existence of an underscreened surface layer with low population of *d*-electrons gives rise to a stronger, compared to classical calculations, local field of surface plasmon collective excitation that determines the magnitude of Raman signal from a molecule near the surface. Although the dominant finite-size effect is still a reduction of SERS due to surface plasmon damping, the decrease of the Raman signal is considerably slower when the surface layer effect is taken into account.

We calculated the size-dependence of SERS in the framework of two region model with different (but classical) distributions of *sp*-band and *d*-band electron densities and semiclassical treatment of electron surface scattering, and found that the additional enhancement becomes stronger as the particle radius decreases. Although for particles size smaller than 2-3 nm, the semiclassical model is no longer valid, the physical mechanism of the enhancement persists for even smaller sizes. In fact, the semiclassical model underestimates the fraction of underscreened region as the particle size decreases. On the other hand, in the absence of a sharp boundary the local fields are weaker. The outcome of this competition depends on the precise shape of the electron density as well as on the surrounding dielectric. A fully quantum-mechanical calculations of SERS will be presented in a subsequent publication [37].

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